Form Approved REPORT DOCUMENTATION PAGE OMB No. 0704-0188 Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for falling to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS. 1. REPORT DATE (DD-MM-YYYY) 2. REPORT TYPE 3. DATES COVERED (From - To) Technical Papers 4. TITLE AND SUBTITLE 5a. CONTRACT NUMBER ease see 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER 6. AUTHOR(S) 5d. PROJECT NUMBER 2303 5e. TASK NUMBER M208 5f. WORK UNIT NUMBER 3*45 709* 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) 8. PERFORMING ORGANIZATION REPORT Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) 10. SPONSOR/MONITOR'S ACRONYM(S) Air Force Research Laboratory (AFMC) AFRL/PRS 11. SPONSOR/MONITOR'S 5 Pollux Drive NUMBER(S) Please see attached Edwards AFB CA 93524-7048 12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited. 13. SUPPLEMENTARY NOTES 14. ABSTRACT 20030129 234 15. SUBJECT TERMS

17. LIMITATION

OF ABSTRACT

18. NUMBER

OF PAGES

16. SECURITY CLASSIFICATION OF:

b. ABSTRACT

Unclassified

c. THIS PAGE

Unclassified

a. REPORT

Unclassified

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MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO)

17 May 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-VG-2002-118

Jerry Boatz (PRSP) et al., "New Materials Design" (Viewgraphs)

DoD Users Group Conference (Austin, TX, 10-14 June 2002) (<u>Deadline: 07 June 2002</u>) (Statement A)

1. This request has been reviewed by the Foreign Disclosure (b.) military/national critical technology, c.) export controls or d.) appropriateness for release to a foreign nation, and e.) tech Comments:	distribution restrictions, unical sensitivity and/or economic sensitivity.
Signature	Date
2. This request has been reviewed by the Public Affairs Office and/or b) possible higher headquarters review. Comments:	e for: a.) appropriateness for public release
Signature 3. This request has been reviewed by the STINFO for: a.) chab) appropriateness of references, if applicable; and c.) format Comments:	Date nges if approved as amended, and completion of meeting clearance form if required
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APPROVED/APPROVED AS AMENDED/DISAPPROVED

PHILIP A. KESSEL Date
Technical Advisor
Space and Missile Propulsion Division

New Materials Design DoD UGC, 10-14 Jun 02 Austin, TX



Jerry Boatz

Senior Research Chemist Propulsion Directorate Air Force Research Laboratory



NEW MATERIALS DESIGN



THE TEAM...

Prof. Mark S. Gordon

Prof. Gregory Voth



Prof. Sharon Hammes-Schiffer



Dr. Ruth Pachter, AFRL/MLPJ



Dr. Jerry Boatz, AFRL/PRSP



OUTLINE

1. Project Overview

- High energy density matter
- Polyhedral oligomeric silsesquioxanes (POSS)
- Non-linear optical materials

2. Theoretical Methods and benchmarks

- Ab initio electronic structure theory
- Nuclear-electronic orbital approach
- Centroid Molecular Dynamics

3. Results

4. Summary

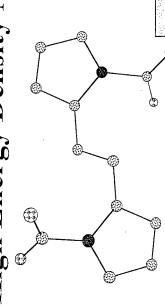




PROJECT OVERVIEW - HEDM



High Energy Density Matter -- next generation rocket propellants



High-nitrogen/polynitrogen compounds



Specific Impulse

Atom-doped solid hydrogen



PROJECT OVERVIEW - HEDM



Technical issues being addressed using CCM

1. High-nitrogen/polynitrogen compounds

Objective: identify, characterize, and synthesize stable compounds with high heats of formation, high densities

- structures, energy content, stabilities, reaction pathways

2. Energetic atoms in solid hydrogen

Objective: stabilize ~5% energetic atoms in solid hydrogen

stabilities, mobilities, concentration limits of atoms stored in hydrogen matrices



PROJECT OVERVIEW - POSS



Polyhedral oligomeric silsesquioxanes -- next generation plastics

Molecular Silica

Organo-alcohols Organo-halides Chlorosilanes Alkoxysilanes Aminosilanes Styrenics Reactive Group α-Epoxides.▲ Silanes Acrylics Isocyanates Silanols **Phenols** α-Olefins

Mechanical property/viscosity/thermal modifiers Heat/abrasion resistant paints and coatings Crosslinking agents Fire retardants

As Plastics

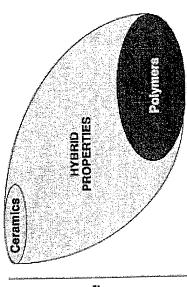
Space resistant resins Electronic materials Packaging/coatings Medical materials Optical Plastics

As Preceramics

Ablative materials (nozzles, insulations etc.) Precursors to glassy or ceramic matrices Claddings/electronics coatings

HYBRID POLYMERS

1.5 nm



Toughness

1.5 nm

Temperature

9



PROJECT OVERVIEW - POSS



Technical issues being addressed using CCM

1. Mechanisms of formation

Objective: rational design and synthesis of POSS

- role of solvents, acid/base catalysis, substituent effects on mechanism of formation

2. Potential applications as molecular "sieves"

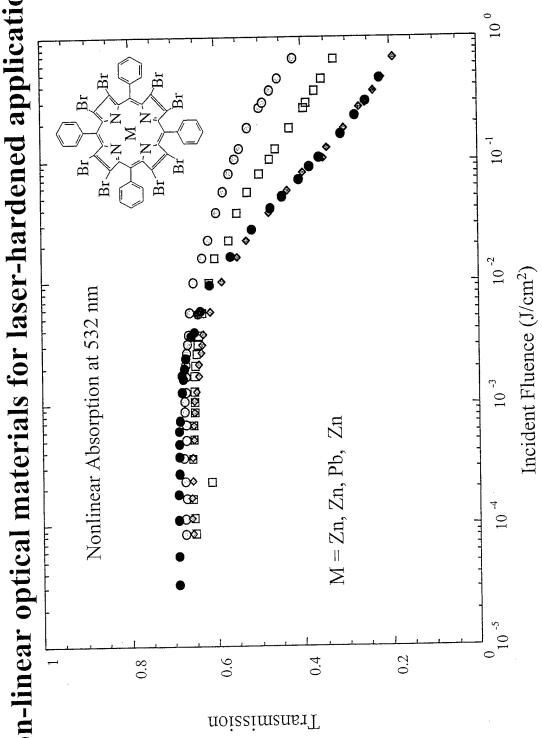
Objective: determine if POSS cages can be used to separate small molecules

- determine barriers to encapsulation of N_2 and O_2

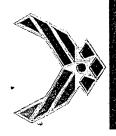
PROJECT OVERVIEW - NLO









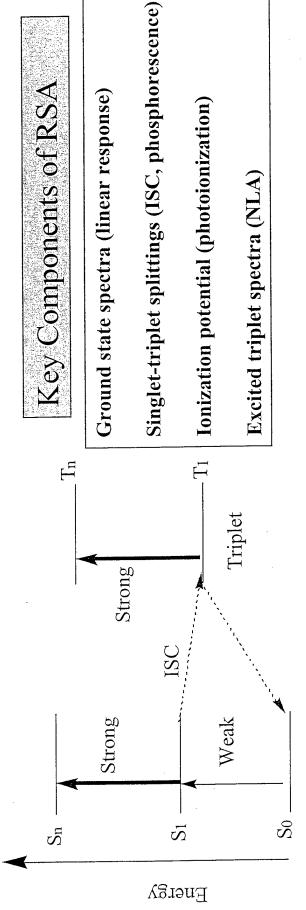


PROJECT OVERVIEW - NLO



Technical issues being addressed using CCM

1. Mechanism of reverse saturable absorption (RSA)



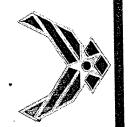
Key Components of RSA

Ground state spectra (linear response)

Ionization potential (photoionization)

Excited triplet spectra (NLA)

Five-level model for nonlinear absorption Singlet



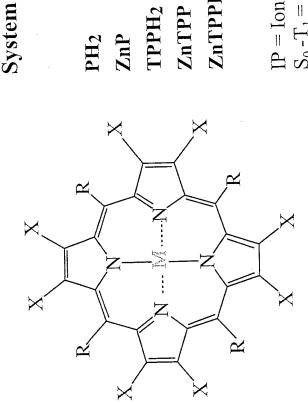
PROJECT OVERVIEW - NLO



Technical issues being addressed using CCM

2. "Tuning" of absorption spectrum by benzannulation, halide substitution

Property



	2	×	~	IIP	S_0 - S_n	S_0 -T1	T_1 - T_n
PH_2	124 124 124 127	Н	H	E, C	E, C	E, C	E, C
ZnP		二	H	E, C	E, C	E, C	E, C
$TPPH_2$		H	-	E, C	E, C	E, C	E, C
ZnTPP		H	· •	E, C	E, C	E, C	E, C
ZnTPPBr8		Br	· - -	C	E, C	E, C	E, C

IP = Ionization Potential, S_0 - S_n = Ground State Spectrum, S_0 - T_1 = Singlet-Triplet Gap T_1 - T_n = Triplet-Triplet Spectrum E = Experiment, C = Calculated





1. Ab initio electronic structure theory

- General Atomic and Molecular Electronic Structure System (GAMESS) -- a CHSSI code
- Nuclear-electronic orbital approach (NEO) for including nuclear quantum effects (important, e.g., in proton transfer reactions)

molecular electronic Schrödinger equation from quantum mechanics: Various computational techniques are employed to solve the

$$\left| -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \sum_{i} \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{i} \sum_{j>i} \frac{1}{r_{ij}} \right| \Psi_{el} = E_{el} \Psi_{el}$$

Categories of approximate solutions:

- a) "Self-consistent field" (SCF): reasonably good geometries
- b) "Electron correlation": post-SCF correction, required for reliable energetics (e.g., barriers).





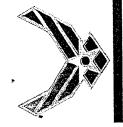
1. Ab initio electronic structure theory (cont.)

"clampled nuclei") approximation -- NOE method treats specified - Most electronic structure codes use Born-Oppenheimer (i.e., nuclei at QM level.

Nuclear-Electronic Hamiltonian

$$H_{\text{tot}}(\mathbf{r}_e, \mathbf{r}_q; \mathbf{r}_c) = -\sum_{i}^{N_e} \frac{1}{2} \nabla_i^2 - \sum_{i}^{N_e} \sum_{A}^{N_c} \frac{Z_A}{r_{iA}} + \sum_{i}^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}}$$
$$-\sum_{I}^{N_p} \frac{1}{2M_I} \nabla_I^2 + \sum_{I}^{N_p} \sum_{A}^{N_c} \frac{Z_A Z_I}{r_{IA}} + \sum_{I}^{N_p} \sum_{I}^{N_p} \frac{Z_I Z_J}{r_{IJ}}$$
$$-\sum_{i}^{N_e} \frac{N_p}{I} \frac{Z_I}{r_{iI}} + \sum_{A}^{N_c} \sum_{B>A}^{N_c} \frac{Z_A Z_B}{r_{AB}}$$

 N_e : number of electrons (coordinates \mathbf{r}_e) N_p : number of quantum nuclei (coordinates \mathbf{r}_p) N_c : number of classical nuclei (coordinates \mathbf{r}_c)





Ab initio electronic structure theory

Current Status of parallel GAMESS

	RHF	ROHF	H H	GVB	MCSCF
Energy	dpo	dpo	cdp	cdp	cdp
Analytic Gradient	dpo	cdp	cdp	cqb	dpo
Numeric Hessian	dpo	cdp	cqb	cdp	dpo
Analytic Hessian	cdp	dpo	ı	cdp	
MP2 energy	cqb	dpo	dpo	ı	d O
MP2 gradient	dpo		cq	1	
CI energy	dpo	cdp	•	dpo	cqb
Cl gradient	po	1	1	1	
DFT energy	cqb	cdp	cdb	1	
DFT gradient	cqb	cdp	dpo		
	. (•			

c = conventional disk storage of AO integrals

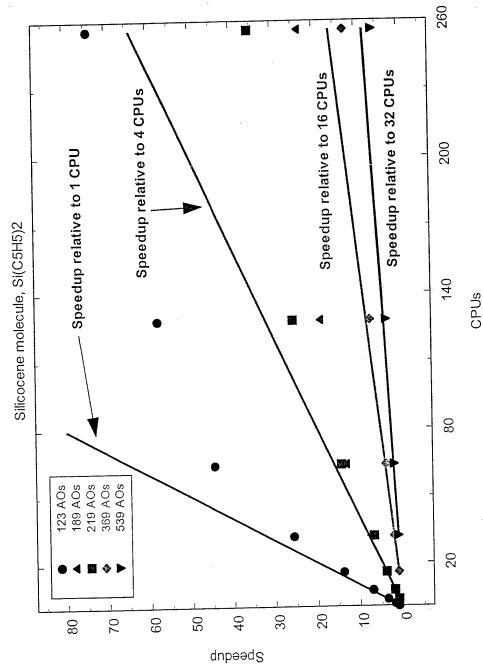
d = direct evaluation of AO integrals

p = runs in parallel

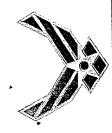


Ab initio electronic structure theory

MP2 Gradient Scalability Test



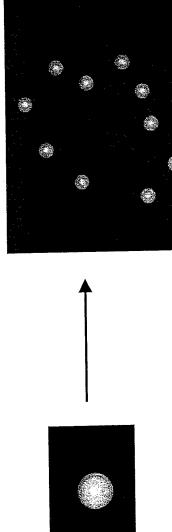


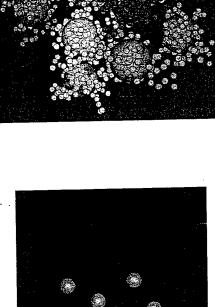


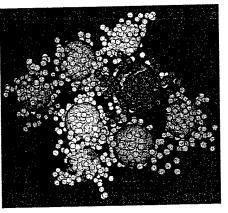


Path Integral Molecular Dynamics & Centroid Molecular Dynamics (CHSSI codes)

Simulation methods based on path integral techniques for mapping quantum particles onto "polymer ring" of classical quasiparticles:





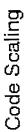


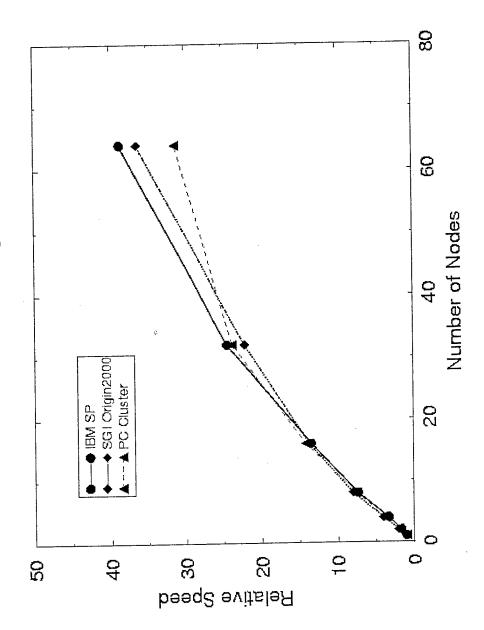
classical dynamics done on collection of quasiparticles => natural, Each "real" particle is replaced by N (50<N<500) quasiparticles; efficient parallelism.





Path Integral Molecular Dynamics & Centroid Molecular Dynamics







Input>rocket, chamber, 20.410000, exhaust, 0.010000

Rocket specific impulse calculation:

The chamber pressure = 20.41 atm The exhaust pressure = 0.01 atm

The initial equation error was huge: 24728.149173

The Chamber State:

Reference state = reactants H(R) = H-1773.07, E(R) = E-1773.05, S(R) = S-0.00

VGS S(R) E(R)V \mathbf{T} H(R)P . (CAL/GM) (CAL/K/GM) (CC/GM) (CAL/GM) (K) (CC/GM) (MTM) 2.389 909.6888 -449.64 0.00 6436.6 909.6888 20.4 1.)

Product concentrations

Name (mol/kg) (mol gas/mol explosive)

2.112e+001 5.410e+000 n2 Gas

7.734e+000 1.981e+000 co Gas

4.609e+000 1.180e+000 no Gas

1.561e+000 3.998e-001 o2 Gas

7.513e-002 1.924e-002 co2 Gas

1.418e-003 3.632e-004 no2 Gas

solid 0.000e+000 0.000e+000

3.510e+001 8.990e+000 Total Gas Total Cond. 0.000e+000 0.000e+000

The Exhaust State:

Reference state = reactants H(R) = H-1773.07, E(R) = E-1773.05, S(R) = S-0.00

VGS S(R) E(R)V H(R)Ρ (CAL/GM) (CAL/K/GM) (CC/GM) (CC/GM) (K) (MTA) 2.389565350.1813 2148.9 -1863.53 -2000.43 0.0 565350.1813 1.)

Product concentrations

Name (mol/kg) (mol gas/mol explosive)

2.337e+001 5.984e+000 n2 Gas

6.157e+000 1.577e+000 co2 Gas

1.652e+000 4.232e-001 co Gas 7.645e-001 1.958e-001

o2 Gas 3.160e-002 1.234e-001

no Gas

5.283e-006 1.353e-006 no2 Gas *c solid 0.000e+000 0.000e+000

3.206e+001 8.212e+000 Total Gas

Total Cond. 0.000e+000 0.000e+000

The specific impulse = 402.54 seconds



RESULTS - HEDM



High-nitrogen/polynitrogen compounds

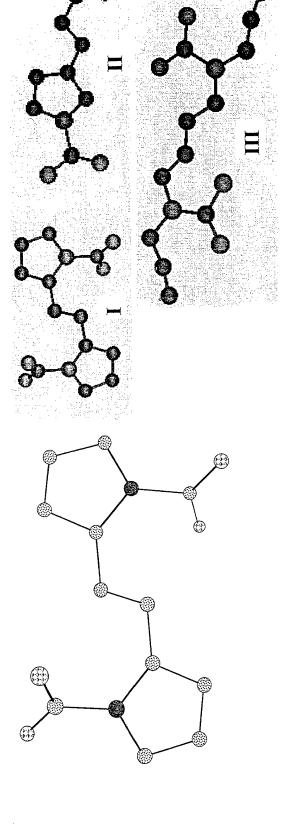
Predicted $\Delta H_f = 457 \text{ kcal/mol}$, $I_{sp} = 329 \text{ sec (sea level)}$

 $(I_{sp} \text{ for hydrazine} = 233 \text{ sec})$

Relative energies (kcal/mol)

I: 0 II: -15

III: +36

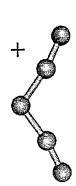


Computational requirements: 4500 MW memory, ~350,000 node-hrs, ERDC T3E

tCCSD(T)/6-311+G(2d) results



Comparison of Calculated and Measured Spectra Identifying a Completely New Molecule:



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	15N_14N_14N_14N_14N]+ASF ₆ - and 14N_14N_15N_14N_14N]+ASF ₆ -
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<u>Calc.</u>†

<u>Obs.</u>

<u>Mode</u>

14N - 15N Isotopic Shifts (cm⁻¹)

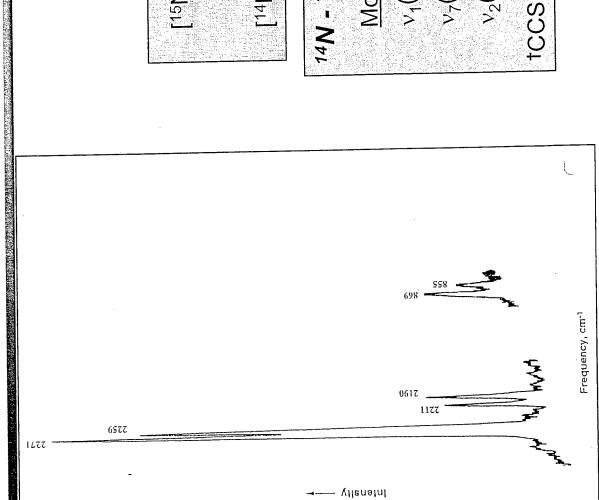
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7

 $v_1(a_1) = v_2(b_2)$

 $v_2(a_7)$

2. 4:





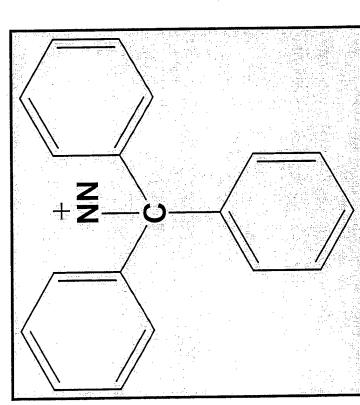




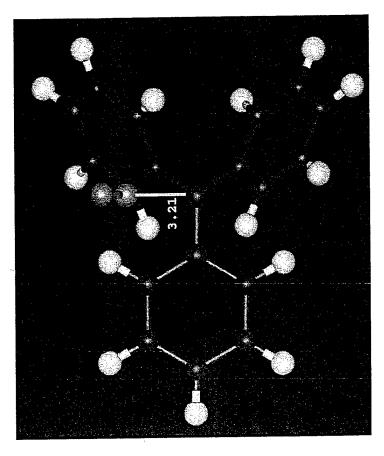
Identifying Precursors for New Polynitrogens



This ion has been suggested as a useful precursor to new polynitrogen molecules...



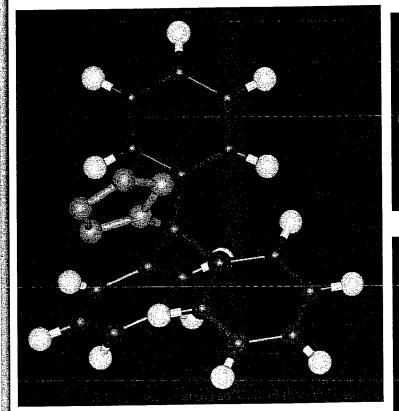
... but calculations predict it to be unstable.

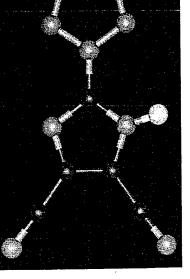


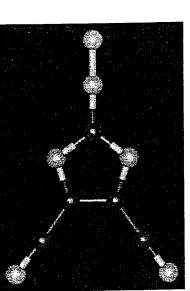
Computational requirements: ~10,000 CPU-hours, 1200 MW on IBM SP/P3 at ASC

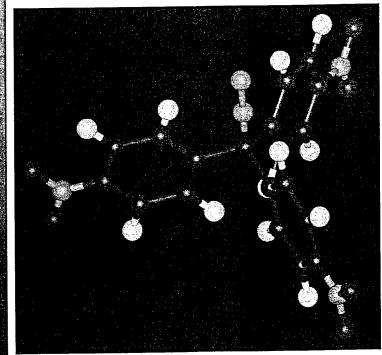
Other Potential Polynitrogen Precursors Being Investigated



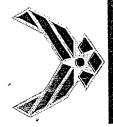










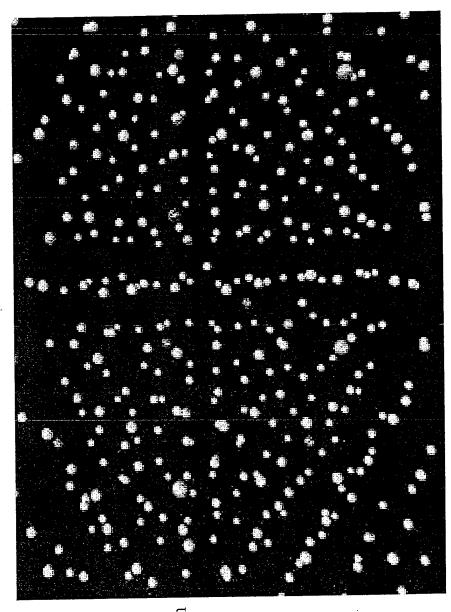




6.25% B atoms in solid para-H₂

Previous key results

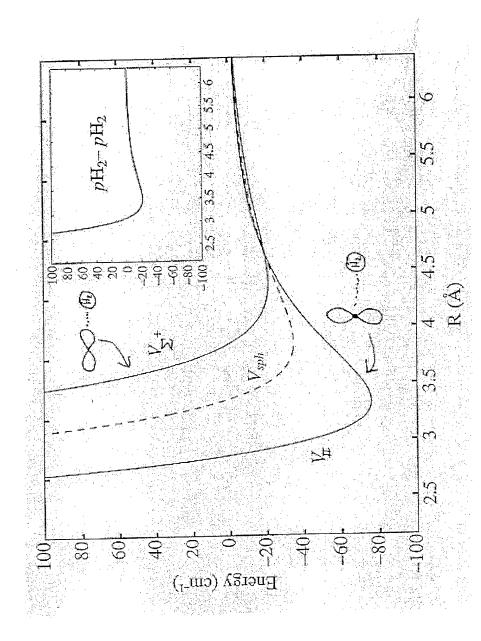
- 1. In sH_2 , B atoms more stable than Li atoms
- 2. No recombination of B atoms seen at concentrations up to 6.25%.
- 3. "Forced" recombination of B atoms does not trigger phase separation.







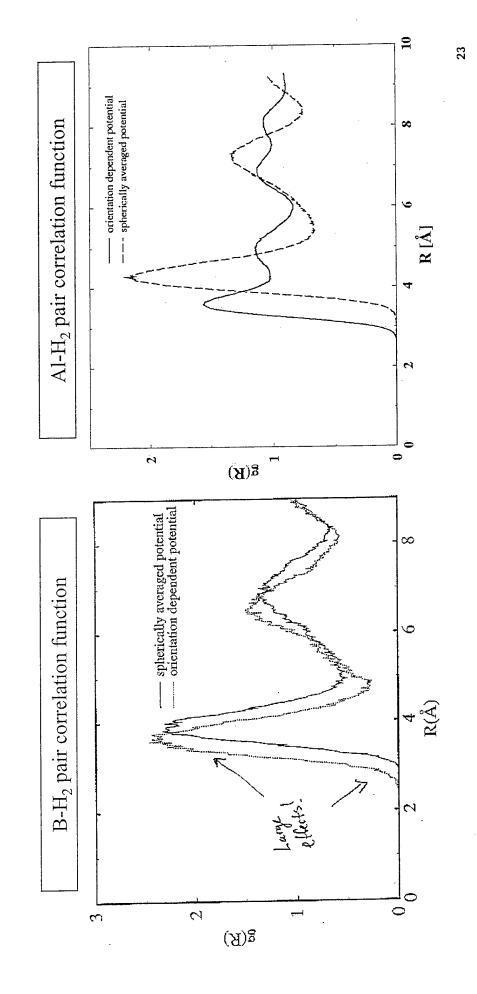
How important is the orientational dependence of B-H₂ (Al-H₂) interactions in $B/sH_2 (AI/sH_2)$?













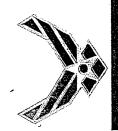


B-H₂ and Al-H₂ interaction energies (cm⁻¹)

$<$ V $_{A}$ - H_{2} >	546.72 (1.92)	.443,32 (1.92)	-538.49 (6.06) -273.86 (2.37)	439.88 (3.56), -179.52 (4.90)
	263.2		-273	-179,
^ 7	(1.92)	(1.92) (1.92)	(0.06)	(3.56)
<vb-h<sub>2></vb-h<sub>	-546.72	-443,32	-538.49	-439.88
	Orientation dependent	Spherically averaged	Orientation dependent	Spherically averaged
	Impurity	no defect	Impurity & defect	

Krumrine, J.R., Jang, S., Alexander, M.H., and Voth, G.A.: J. Chem. Phys. 113 (2000) 9079

Mirijanian, D.T., Alexander, M.H., and Voth, G.A.: To be published





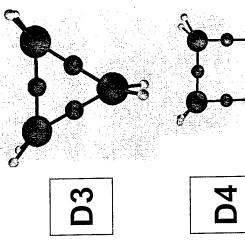
Mechanism of formation

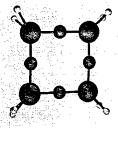
Key steps

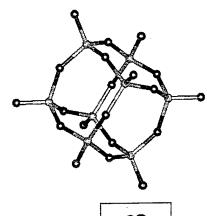
- 1. Hydrolysis of RSiX, (R=H,CH₃,t-butyl,etc.; X=Cl) $RSiCl_2OH + H_2O \rightarrow RSiCl(OH)_2 + HCl$ $RSiCl_3 + H_2O \rightarrow RSiCl_2OH + HCI$ $RSiCl(OH)_2 + H_2O \rightarrow RSi(OH)_3$
- $2 \text{ RSi(OH)}_3 \rightarrow \text{R(OH)}_2 \text{SiOSi(OH)}_2 \text{R} + \text{H}_2 \text{O}$ 2. Condensation of RSi(OH)₃ to disiloxane
- $RSi(OH)_3 + R(OH)_2SiOSi(OH)_2R \rightarrow D_3 + 2H_2O$ 3. Condensation of disiloxane to D_3,D_4

[3+1]: RSi(OH)₃ + R(OH)₂SiOSi(OH)₂R \rightarrow D₄ + 2H₂O Ring.Expansion: $RSi(OH)_3 + D_3 \rightarrow D_4 + H_2O$ [2+2]: 2R(OH), SiOSi(OH), $R \rightarrow D_4 + 2H$, O

4. Condensation of D_3 , D_4 to POSS (in progress) $2D_4 \rightarrow T_8 + 4H_2O$











Mechanism of formation: role of solvent (H2O) & substituents (R)

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I(OH) ₂ R		#@#	3)	3.3)	(6)	o.4)	italyzed
4) ₂ SiOS	cal/moll	MP2/6-31/G*	10.9 (-9.3)	7.7 (-13.3)	9.8 (-9.3)	(r.9 (=10.4)	vater-ce
RSi(OH)3 + RSi(OH)3 ->R(OH)2SiOSi(OH)2R + H2O	Energy barrier (kcal/mol)			1.7)	4.9)	(7') (7')	Values in parentheses are for water-catalyzed results
(S)(OH)	ergy ba	HF/6-31G"	30.4 (16.7)	28.2 (14.7)	34.3 (24.9)	31.1 (18.2)	heses
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RSI	. α *			Ü	f-Bu		aluesir
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Catalyzed by a water

Catalyzed by a water

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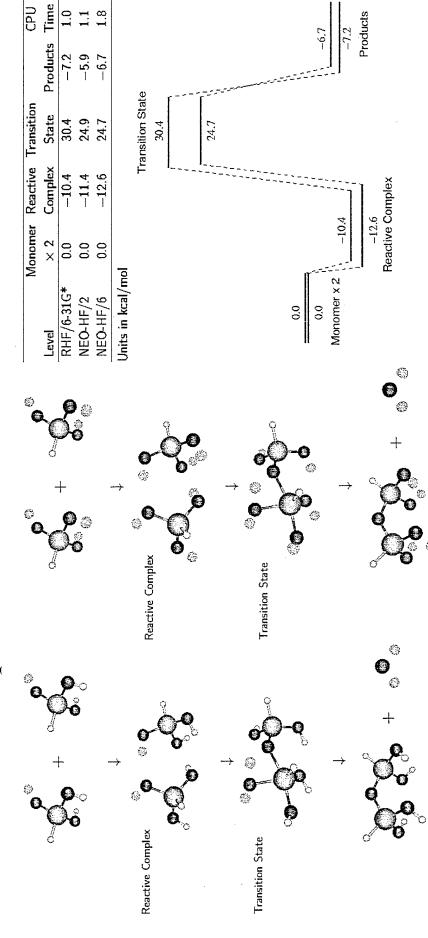
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Nuclear quantum effects in condensation reactions



Hammes-Schiffer, S.: J. Phys. Chem. A 102 (1998), 10443

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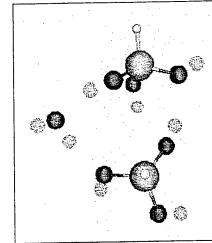
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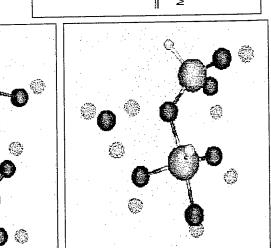




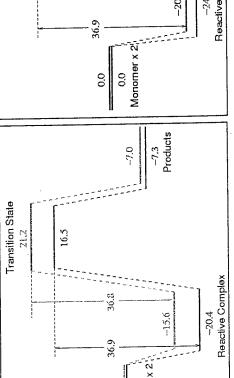
Nuclear quantum effects in water-catalyzed condensation reactions

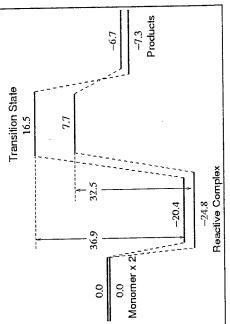
$2 \times HSi(OH)_3 + H_2O \rightarrow H(OH)_2Si-O-Si(OH)_2H + 2H_2O$





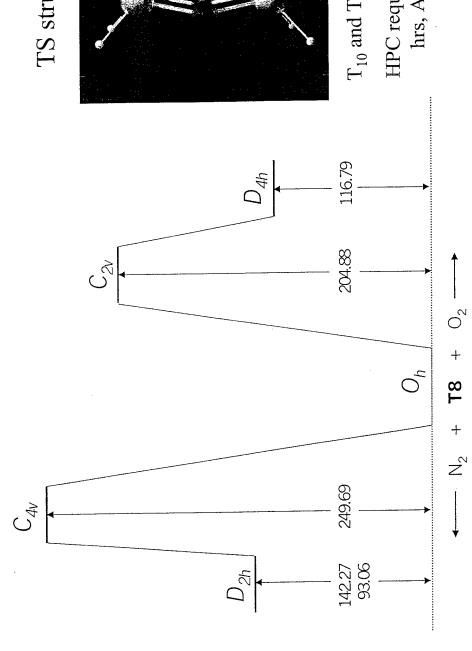
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UHF/6-31G*	-20.4	16.5	-7.3	1.0
3HF/6-31G*/ZPE	-15.6	21.2	-7.0	
VEO/HF/4	-23.0	7.2	-5.9	1.1
	-24.8	7.7	-6.7	1.8



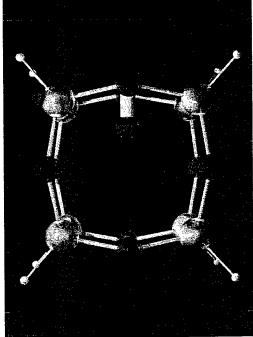




Molecular "sieves": preferential capture N2 vs. O2?







 T_{10} and T_{12} calculations in progress HPC requirements: ~50,000 nodehrs, AHPCRC T3E, 256 GB





RESULTS - NLO

B3LYP S₀-T₁ Excitation Energies (in eV)

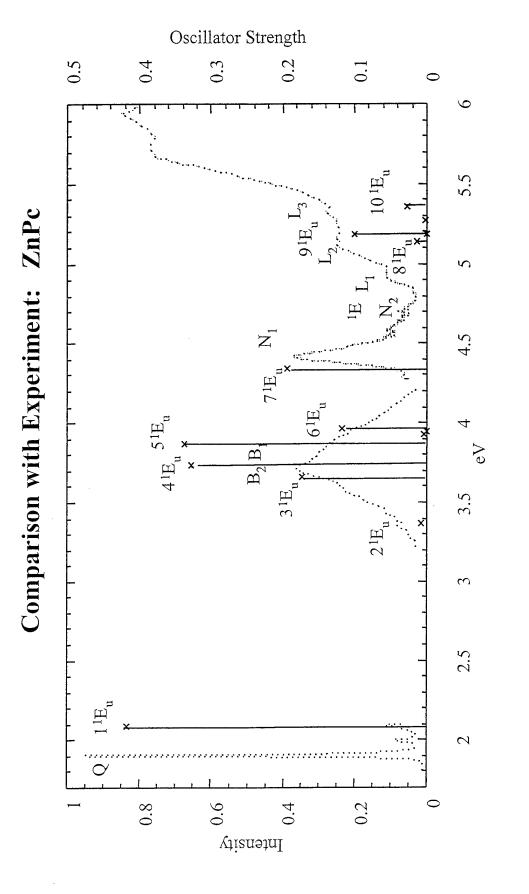
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System	6-31G(d)	Error	Exp
Porphyrin (1 ³ B _{2u})	1.42	0.16	1.58^{a}
Zinc Porphyrin (1 ³ B _{1u})	1.65	0.07	1.72b
Tetraphenylporphyrin (1 ³ B ₁)	1.31	0.14	1.45 ^c
Zinc Tetraphenylporphyrin(1 ³ B ₁)	1.53	90.0	1.59d
Zinc Phthalocyanine (1 ³ B _{2u})	1.05	80.0	1.13e
Zinc Tetrabenzporphyrin (1 ³ B _{1u})	1.41	0.16	1.57f
Phthalocyanine (1^3B_{1u})	1.18	90.0	1.248
Mean Error		0.10	

Gouterman, J. Mol. Spectrosc. 1971, 39, 421 (octane at 77 K) EMcVie et al., J. Chem. Soc. Faraday Trans. II 1978, 74, ether to ethanol at 77 K) eVincett et al., K. E. J. Chem. Phys. 1971, 55, 4131. (1-chloronapthalene at 77 K) fBajema, ^aGouterman, Khalil, J. Mol. Spectrosc. 1974, 53, 88. (EPA (5:5:2) mixture of ethyl ether to isopentane to ethanol Khalil, J. Mol. Spectrosc. 1974, 53, 88. (EPA at 77 K) dWalters et al., J. Phys. Chem. 1995, 99, 1166.(1:1 mixture of and 50% ethyl iodide at 77 K) ^bGradyushko, Tsvirko, Opt. Spectrosc. 1971, 31, 291.(EPA at 77 K) ^cGouterman, 1870 (1-chloronapthalene at 77 K)

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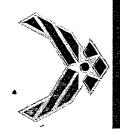


RESULTS - NLO





HPC Requirements: ~100,000 CPU hours, on SGI O2K + IBM SP3 + SGI O2K @ ASC



SUMMARY



High Energy Density Matter

- High-nitrogen/polynitrogen compounds are more energetic than hydrazine.
- Trityldiazonium cation is not a stable polynitrogen precursor.
- Inclusion of anisotropic interactions of B, Al atoms in sH2 predict greater stability than spherical interaction model.

Polyhedral Oligomeric Silsesquioxanes (POSS)

- Proton transfer reactions for hydrolysis and condensation are catalyzed by
- Alkyl substituents (R) in RSiX₃ have minor effects on hydrolysis and condensation reaction barriers.
- Nuclear quantum effects are important in proton transfer reactions -- lower barriers by >5 kcal/mol.
- T_8 is too small to encapsulate N_2 or O_2 .



SUMMARY (cont.)

NLO materials

- Time-dependent density functional theory accurately predicts NLA in porphyrins.
- Computed triplet-triplet excitation energies within 0.1-0.4 eV of experiment
- Computed singlet-triplet excitation energies within 0.1-0.2 eV of experiment
 - Computed ionization potentials accurate within 0.1 eV of experiment





ACKNOWLEDGEMENTS



POSS: Takako Kudo, Shawn Phillips, Simon Webb, Frank Feher, Joe Lichtenhan

HEDM: Millard Alexander, Jennifer Krumrine, Soomin Jang, Jeff Mills, Jeff Sheehy, Don Thompson, Dan Sorescu

NLO: Kiet Nguyen, Paul Day

GAIMESS: Graham Fletcher

MSRCs, DCs: ASC, ARL, ERDC, NAVO, MHPCC, AHPCRC, ARSC, AFFTC

CHSSI funding (CCM-2, CCM-4, MBD-01)